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Local density functional study on adsorption of Cu^{2+} and Fe^{2+} on a Si(100) surface

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Abstract

Using a local density functional calculation, we investigate the adsorption energies, geometries and electronic structures of single Cu^{2+} and Fe^{2+} ions on a Si(100) surface. The adsorption energy results reveal that both ions are stably adsorbed in a hollow site; from this site, Cu^{2+} is located at 0.51 Å and Fe^{2+} is located at 0.41 Å from the surface, respectively. The adsorption energy of Cu^{2+} is about 1.5 times larger than that of Fe^{2+}. This means that Cu^{2+} is strongly adsorbed on the silicon surface. From the analysis of spin density, we find that Cu^{2+} strongly attracts the electrons of the silicon surface, because spin density is delocalized in the silicon backbone. As a result, the 3d orbital of Cu^{2+} becomes more similar to the closed-shell state compared to that of Fe^{2+}. This means that the core electronic state of Cu^{2+} is closer to the neutral atom, which is qualitatively confirmed by XPS measurements.

1. Introduction

The interactions between metals and silicon surfaces play an important role in semiconductor technology. For example, the chemical vapor deposition (CVD) technique, being one of typical silicon surface reactions, is widely used for epitaxial crystal growth on the surface [1]. This reaction is equivalent to a catalytic reaction in the sense that the chemical reagent is decomposed on the surface. Also, it is important in preventing the adsorption of trace metal contaminants on the silicon wafer, because these contaminants affect the quality of electronic devices, especially very large-scale integrated (VLSI) circuits. Many efforts have been made so far in order to develop an effective technology to prevent this metal adsorption. Yet no technique has been proposed beyond the present RCA cleaning technique, developed about 20 years ago [2].

As for the adsorption behavior of trace metal contaminants, it is well known that there is a marked difference between Cu^{2+} and Fe^{2+}. For example, copper tends to deposit on the wafer surface after washing it with the acidic liquid chemicals polluted by trace metal contaminants [3]. Thus, the adsorption behavior of trace metal contaminants depends on the pH of the liquid chemicals or the surface states of the Si wafer. As the accuracy of trace analysis is well-developed, the experimental data on the behavior of such contaminants are reported from a phenomenological point of view. The purpose of this paper is to investigate the adsorption mechanism of the contaminants using quantum chemical calculations, which are powerful tools, in order to give a theoretical explanation to such experiments [4], and to study the nature of the metal–silicon interaction.

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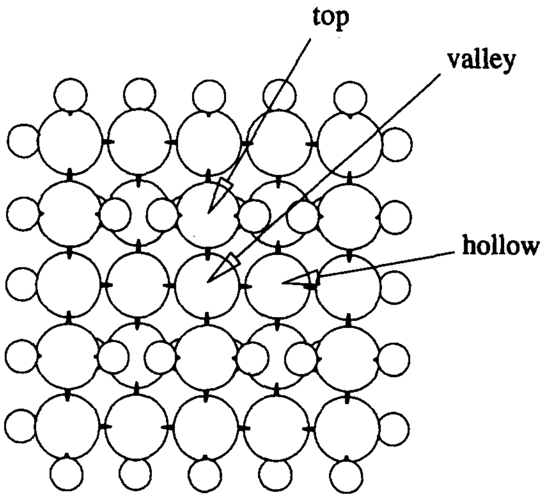

Fig. 1. Three adsorption sites of the Si(100) model. All dangling bonds are terminated with hydrogen atoms. Large and small circles stand for Si and H atoms, respectively.

In this article, we discuss the adsorption energies, geometries and the electronic structure of the adsorption state of Cu^{2+} and Fe^{2+} on a hydrogen terminated Si(100) surface, using a density functional approach.

2. Method of calculation

In this work, we use the density functional program 'DGauss' [5], developed by the CRAY UniChem Project, for the calculation of adsorption energies, geometries and electronic structure. Energy calculations are based on a local spin density approximation [6], neither including nonlocal correction nor geometry optimization. The Vosko–Wilk–Nusair (VWN) exchange-correlation potential [7] is used throughout this calculation. Pseudo-potentials, which are generated by the method of Troullier and Martins [8], are used for Si and Cu^{2+}/Fe^{2+}. Basis sets contain 2 contracted s orbitals, 1 contracted p and d orbital for Si, and 3 contracted s, 1 contracted p and 2 contracted d for Cu^{2+}/Fe^{2+} [9].

We use hydrogen terminated Si(100) 1 × 1 surfaces as the model clusters, which correspond to the surface state washed by acidic liquid chemicals [10]. In these models, we adopt the symmetric dihydride structure and do not take account of the reconstructed structure [11]. In addition, we suppose three adsorption sites, as shown in Fig. 1; we define the sites as top, valley and hollow, respectively. In our calculation, small clusters containing 15 Si atoms, 24 H atoms and 1 Cu^{2+}/Fe^{2+} ion are used for each adsorption site (Fig. 2). All our model clusters take into account fourth silicon layers. The potential energy is calculated by changing the vertical distance between the metal ion and the first silicon layer.

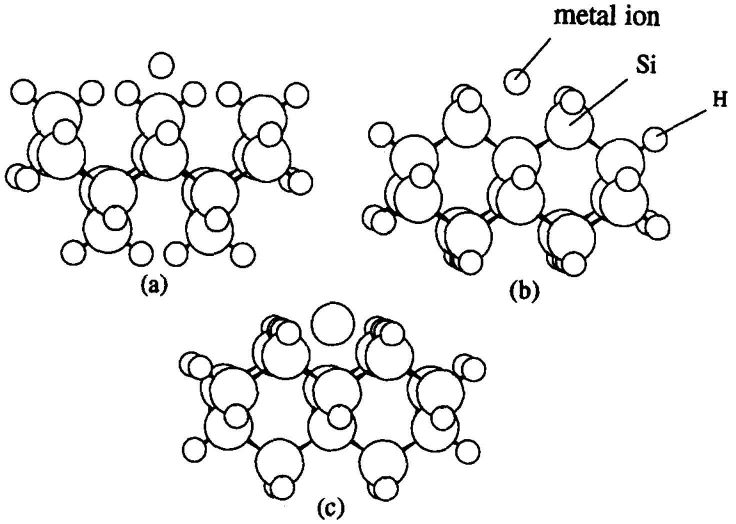

Fig. 2. Three small clusters for each adsorption site (side view). All dangling bonds are terminated with hydrogen atoms. These clusters consider the fourth silicon layer. (a) Top site; (b) valley site: (c) hollow site.

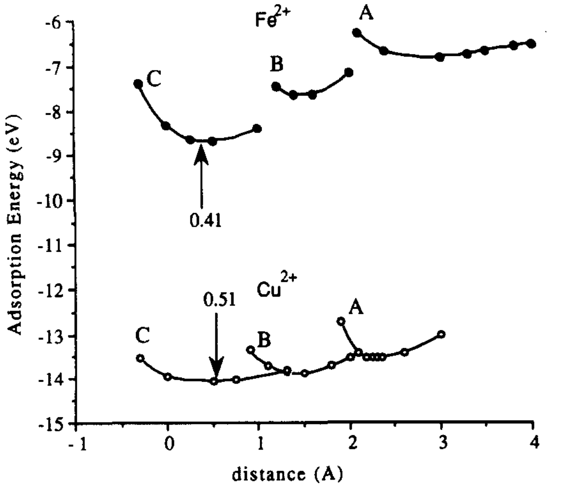

Fig. 3. The potential energy plot of Cu^{2+} and Fe^{2+}. The line containing open circles stands for Cu^{2+} adsorption and the line with filled circles stands for Fe^{2+}. The three adsorption sites are labelled: (A) top site; (B) valley site; (C) hollow site. The distance is measured from the first silicon layer. The energy minimum in the hollow site is indicated by the arrows.

The adsorption energy is defined as the difference between the total energy of the whole cluster and the sum of the total energy of one metal ion and the silicon cluster:

$$\Delta E = E_{\text{tot}}\,(\text{adsorbed cluster}) - (E_{\text{tot}}\,(\text{cluster}) + E_{\text{tot}}\,(\text{ion})) \quad (1)$$

3. Results and discussion

The energy calculation reveals that both Cu^{2+} and Fe^{2+} are adsorbed in the hollow site in their ground states as shown in Fig. 3. The equilibrium height is 0.51 Å for Cu^{2+} and 0.41 Å for Fe^{2+}. It is a little longer in Cu^{2+}. This attributes that, in the hollow site, the ionic radius of Cu^{2+} is larger than that of Fe^{2+}. We confirm that Cu^{2+} has a larger ionic radius than Fe^{2+} from an analysis of the electron density map. Also, the difference of the ionic radius suggests that Cu^{2+} more easily attracts electrons from the cluster, compared to Fe^{2+}.

The adsorption energy of Cu^{2+} is about 1.5 times larger than that of Fe^{2+}, namely −14.15 eV and −8.68 eV, respectively. This result suggests that Cu^{2+} is adsorbed more stronger on the silicon surface. In addition, the curvature of the adsorption potential of Cu^{2+} is less steep even at 0 Å than Fe^{2+}. The energy increase at 0 Å is 0.22 eV (5.5 kcal/mol) and 0.37 eV (8.4 kcal/mol) for Cu^{2+} and Fe^{2+}, respectively. The result for our adsorbed Cu^{2+} system is very similar to that of Freeman and co-workers where the copper atoms easily penetrate into the silicon crystal [12]. They found 6 kcal/mol as the value of the vertical diffusion barrier. Our result also supports the fact that copper has the largest diffusion rate value [13].

Fig. 4 shows the spin density in both Cu^{2+} and Fe^{2+}. The spin density of our Fe^{2+} system is almost localized on the metal ion. However, that of the Cu^{2+} system is considerably delocalized in the silicon backbone. This result shows that a hole

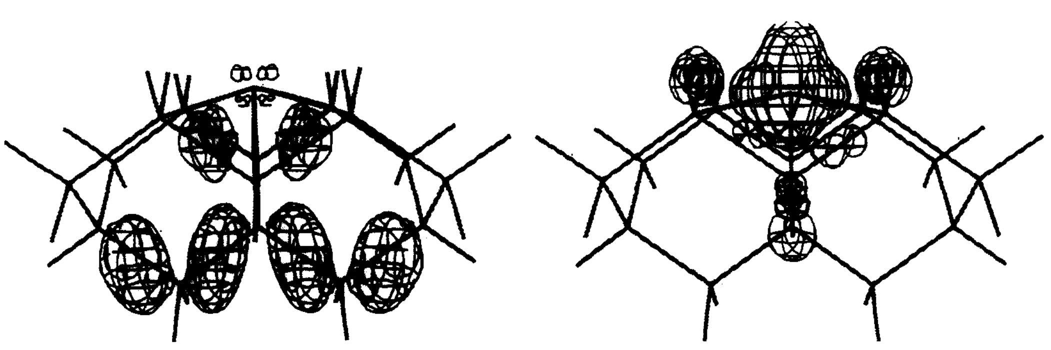
(a) (b)

Fig. 4. The spin density in the hollow site. (a) and (b) show the adsorption of Cu^{2+} and Fe^{2+}, respectively. Solid lines stand for the bond of the cluster. Metal ions are located at the top–center of each cluster. The threshold of the spin density is 0.01.

Table 1
Calculated 2p orbital energy of copper. The values of the neutral and the 2+ state were estimated from the calculation for a single atom

	Adsorbed state	Neutral state	2+ state
ϵ 2p (eV)	−909	−907	−912

of d orbital of Cu^{2+} is transferred to the silicon cluster. This means that charge transfer from the silicon cluster to Cu^{2+} arises more easily than Fe^{2+} as mentioned earlier. Consequently, the characteristics of the open-shell of Cu^{2+} is almost lost. This is confirmed from the density of states (DOS) of the ion. The 3d DOS of Fe^{2+} is split into an up and a down spin. However, this kind of splitting is not observed in the Cu^{2+} cluster system.

The results of the net charge analysis also show the strong electron attraction by Cu^{2+}. The net charges are in the hollow site −0.131 and +0.417 on Cu^{2+} and Fe^{2+}, respectively. We find that the silicon backbone is weakened by the adsorption of Cu^{2+} in the hollow site from an analysis of the electron density map. These results suggest that Cu^{2+} has a high activity as an oxidative catalyst.

Such a drastic change in valence electron density should be reflected on the core electronic state of Cu^{2+}. As the pseudo-potential calculation does not give information about the core electronic state, we recalculated the electronic structure of Cu^{2+} at the adsorption energy minimum in the hollow site with full electronic basis sets (DZVP), and compared the 2p orbital energy of Cu^{2+} in the model cluster with that of the neutral atom and Cu^{2+}. The results are shown in Table 1. Each value of the 2p orbital energy is measured from the highest occupied molecular orbital (HOMO). The 2p orbital energy of Cu^{2+} in the hollow site is closer to that of the neutral atom. The core electronic state is certainly changed by adsorption. This is qualitatively in good agreement with the results of the XPS measurements shown in Fig. 5. The binding energy of the core electron in adsorbed Cu^{2+} on the silicon surface shows the neutral state features, and the satellite peak which is related to Cu^{2+} disappears.

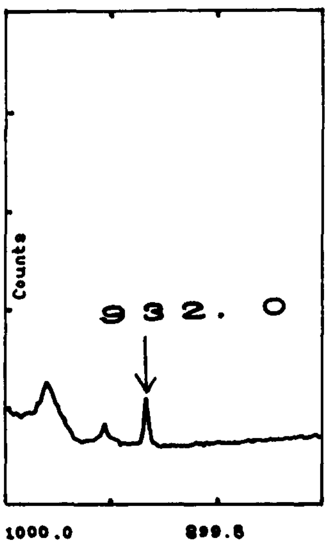

Fig. 5. The XPS profile of Cu deposited on the silicon wafer. The peak at 932.0 eV shows the binding energy of the Cu 2p core electron.

4. Conclusion

We have discussed the adsorption energies, geometries and electronic structure of a single Cu^{2+} and Fe^{2+} ion on the hydrogen terminated Si(100) surface. The adsorption energy reveals that Cu^{2+} is more strongly adsorbed on the Si surface compared to Fe^{2+}. Then, we have shown that a hole of d orbitals of Cu^{2+} is transferred to the silicon cluster by electron migration. It is confirmed from the analysis of the spin density, the density of states and a comparison between the results of 2p orbital energy and XPS measurements. These results suggest that Cu^{2+} has higher activity as an oxidative catalyst, compared to Fe^{2+}.

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